

## PATENT SPECIFICATION

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The Inventor of this invention in the sense of being the actual deviser thereof within the meaning of Section 16 of the Patents Act 1949 is:—FRANCISZEK OLSZOWSKI, Route, 1 Freeport, County of Brazoria, State of Texas, United States of America, a citizen of the United States of America.

## COMPLETE SPECIFICATION

## Process for producing Expanded Graphite

We, THE DOW CHEMICAL COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Midland, County of Midland State of Michigan, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to a process for preparing expanded graphite of a low bulk density.

Loose, low bulk density, vermicular (worm-like) expanded graphite can be used, for example, as a sound proofing medium, a fire stop in partition walls or floor channels, a low density filler for flotation gear, a packaging and/or cushioning medium and a filtration aid for separating finely divided solids suspended in a liquid.

The present invention provides a novel process whereby such an expanded graphite of low bulk density can be prepared employing relatively low expansion temperatures and without the use of hard-to-handle concentrated or fuming oxy-acids.

The present novel process comprises anodically electrolyzing natural crystalline lump or natural crystalline flake graphite in an aqueous electrolyte and heating the so-treated graphite at a temperature of at least about 150°C.

More particularly, the present process comprises anodically electrolyzing a natural crystalline flake graphite or natural crystalline lump graphite in an aqueous acid or aqueous salt electrolyte at an electrolyte temperature of from about 0 to about 80°C., preferably from about 20 to about 50°C., at a cell potential at a minimum of about 2 volts. Ordinarily for most efficient economical operation a maxi-

imum of about 10 volts is employed in the cell. The quantity of electricity passed is equivalent to from about 10 to about 500 ampere-hours per pound (22 to 1100 amp. hrs./kg.) of graphite, and preferably from about 20 to 200 ampere-hours per pound (44 to 440 amp. hrs./kg.) of graphite.

The electrolytically treated graphite is separated from the electrolyte solution and heated at a temperature of from about 150°C. to about 1500°C., or higher, and preferably at a temperature of from about 200°C. to about 1000°C., generally for a period of from less than about 1 second to about 30 seconds or more. The electrolytically treated graphite material can be placed in a suitable reactor or crucible, for example, and subjected to an elevated temperature as produced by an exterior heat source or furnace to achieve the expansion. Direct contact of the treated material with the flame of a propane-air torch or an oxyacetylene torch, for example, also can produce the desired product.

An unexpected advantage of the present process is that the apparent bulk density of the resulting expanded product can be determined to a considerable extent by the total amount of electrolysis and/or the temperature of expansion.

As the total amount of current increases over the range set forth herein the apparent bulk density in the expanded product decreases. Further, as the temperature of expansion increases over the operative range, the apparent bulk density of the expanded graphite product decreases.

The graphite can be expanded in free form or can be incorporated into various inorganic and organic materials prior to expansion for the purposes of imparting special characteristics to these media. To illustrate, light-

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weight flame retardant and/or self-extinguishing compositions can be prepared. Also, light weight compositions having excellent thermal insulating properties and electrical conductivity can be fabricated. Improved refractory and construction units also can be achieved by use of the expanded graphite produced by the present process. The expanded product also finds utility in the formulation of explosives. In some applications, the electrolyzed graphite can be incorporated into other media in the unexpanded form and then be expanded in situ during processing and fabrication.

Graphites suitable for use in the present process are the naturally occurring crystalline flake graphites, as from layered metamorphose rock deposits of Madagascar, and crystalline lump graphites, as from vein deposits in Ceylon. Flake graphite is preferred. Naturally occurring amorphous graphite, e.g. from metamorphose coal beds deposited in Mexico, and synthetic poly-crystalline graphite have been found to be unsuitable for use in the present process. The particle size of graphite to be used is not critical although ordinarily particles of from about 10 to about 200 mesh (U.S. Standard Sieve) (0.074—2.0 mm.) are used for lowest bulk densities. At smaller particle sizes, the apparent bulk density of the final expanded product may be somewhat higher, but may be many times less than that of the unexpanded graphite.

Electrolytes found to be particularly suitable for use in the present process are aqueous acid, ammonium and water soluble metal salt solutions.

Acids particularly suitable are nitric acid, sulfuric acid, hydrobromic acid, phosphoric acid, chromic acid, hydrofluoric acid, perchloric acid, trifluoroacetic acid and mixtures of hydroiodic and hydrochloric acids. These acids can be employed as dilute solutions con-

taining as little as 0.3 weight per cent of the acid member. Ordinarily with the aqueous acid electrolyte solutions from about 1 to about 70 weight per cent of the acid component and preferably from about 10 to about 50 weight per cent acid are employed.

Salts particularly suitable for use as electrolytes in the present process are ammonium, alkali metal and alkaline earth metal salts having nitrate, sulfate, acid sulfate ( $\text{HSO}_4^-$ ), bromate, iodate, chlorate, perchlorate, fluoride, bromide, trifluoro-acetate or a mixture of iodide and chloride as the anion.

The salt electrolyte concentration ordinarily ranges from about 5 weight per cent up to the saturation concentration of the salt in water at the temperature of operation. Preferably, salt solutions at or near saturation are employed.

Both acid and salt solutions less concentrated than indicated can be employed. However, if the electrolyte solution is too dilute, the conductivity may be detrimentally reduced thereby increasing the electrical power required for acid treating the graphite and adversely affecting the economics of operation.

Reactors, material handling equipment, material transporting means and the like equipment to be employed should be constructed of materials that are not detrimentally attacked by the reactants or products and which are operative at the reaction conditions.

The following Examples further illustrate the present invention.

#### EXAMPLE 1

About 20 grams of a commercially available No. 1 grade natural flake graphite having a bulk density of about 59.8 pounds per cubic foot (0.95 g./cc.) was packed into a 25 millimeter diameter by 75 millimeter long porous alumina thimble. The particulate graphite had the following mesh distribution:

Size		
Sieve (U.S. Standard)	mm.	Wt. %
+20	+0.84	19.8
20/30	0.59—0.84	34.7
30/35	0.50—0.59	25.8
35/40	0.42—0.50	7.5
40/50	0.297—0.42	12.2

- 5 A  $\frac{1}{4}$  inch (6.3 mm.) wide strip of platinum was inserted into the graphite flake mass as an electrode connector. This assembly was connected to the positive pole of a battery and the thimble immersed into a saturated aqueous ammonium nitrate electrolyte solution. A  $\frac{1}{4}$  inch (6.3 mm.) diameter graphite rod was used as a cathode to complete the cell.
- 10 The particulate graphite was anodized at a current of 2 amperes at a cell potential of 5.5 volts and electrolyte temperature of about 30°C. The electrolytic reaction was continued for about 15 minutes. During this time
- 15 the graphite flakes were treated by a quantity of electricity equivalent to about 11.5 ampere-

hours per pound (25.3 amp. hrs./kg.) of graphite. A sample of the anodized material was removed from the thimble, placed in a nickel beaker, and heated to a temperature of about 20 400°C. The flakes expanded to yield a particulate worm-like mass having an apparent bulk density of about 0.212 gram per cubic centimeter (i.e. about 13.4 pounds per cubic foot).

25 The remainder of the graphite mass was subjected to further electrolysis, samples being removed at intervals and expanded by heating in a nickel crucible at 400°C. Table I summarizes the apparent bulk densities obtained for the expanded products at various

30 current throughputs.

TABLE I

Sample No.	Current		Product Bulk Density	
	Amp. hrs./lb.	Amp. hrs./kg.	Lbs./cu. ft.	g./cc.
1	11.5	25.3	13.4	0.212
2	23	50.0	2.8	0.045
3	40	88.0	1.3	0.0208
4	200	440.0	0.7	0.0011

- 35 A separate sample of this same anodized product which had received a total treatment of 200 ampere hours/pound (440 amp. hrs./kg.) graphite expanded to provide a product having a bulk density of about 10 lbs/cubic foot (0.16 g./cc.) when heated at 160°C.
- 40 At an expansion temperature of about 200°C. rapid, almost instantaneous expansion of a sample of the electrolyzed material (440 ampere-hours/kg. of graphite) into a mass of discrete elongated worm-like particles having
- 45 an apparent bulk density of about one pound/cubic foot (0.016 g./cc.) was effected.

## EXAMPLE 2

50 A number of salt electrolyte solutions were utilized with the apparatus and following the general procedure described in Example 1 in the anodization of various graphites at a number of current throughputs. The electrolysis was conducted at temperatures ranging from about 55 30 to about 50°C. Cell potentials ranged from about 2.5 volts to about 10 volts. The resulting electrolyzed samples, after separation from the electrolyte, were subjected to heating at a predetermined temperature to provide the

60 vermicular expanded graphite product. Table II summarizes the data and results for a number of runs.

TABLE II

Run No.	Graphite Charge		Electrolyte		Current Throughput Ampere-Hours/ kg. Graphite	Expansion Temp. °C.	Expanded Product Bulk Density g./cc.
	Type	Bulk Density g./cc.	Particle Size (mm.)	Type	Soln. Conc. (Weight % Solute)		
1	Flake	0.95	(1)	NH <sub>4</sub> NO <sub>3</sub>	11.1	99	0.077
2	Lump	1.38	<1.41	"	Sat'd	332	0.077
3	Flake	0.95	(1)	KClO <sub>3</sub>	"	66	0.333
4	Flake	0.95	(1)	"	"	266	0.088
5	Flake	0.95	(1)	"	"	660	0.058
6	Flake	0.95	(1)	"	"	1060	0.0128
7	Flake	0.95	(1)	"	"	1060	0.0064
8	Flake	0.95	(1)	KHSO <sub>4</sub>	11.8	99	0.074
9	Flake	0.61	<0.044	NH <sub>4</sub> ClO <sub>4</sub>	Sat'd	1100	0.029
10	Flake	0.95	(1)	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	11.8	792	0.0106
11	Flake	0.95	(1)	KBrO <sub>3</sub>	11.8	330	0.059
12	Flake	0.95	(1)	"	"	330	0.099 <sup>(2)</sup>
13	Flake	0.95	(1)	KF	Sat'd	282	0.166
14	Flake	0.95	(1)	KBr	"	207	0.115
15	Flake	0.95	(1)	CF <sub>3</sub> COONa	10	234	0.06
16	Flake	0.95	(1)	KI+KCl	21 <sup>(4)</sup>	800	0.066

<sup>(1)</sup> Same mesh distribution as for Example 1.<sup>(2)</sup> Anodized material washed three times with 500-fold excess volumes of water prior to expansion.<sup>(3)</sup> Contacted with propane torch.<sup>(4)</sup> 20 Grams KI and 20 grams KCl per 150 cubic centimeters water.

## EXAMPLE 3

About 5 grams of a commercial No 1 grade natural graphite having an apparent bulk density of about 59.8 pounds per cubic foot (0.95 g./cc.) was placed in a 1-inch (25 mm.) inside diameter by 3-inch (75 mm.) high polytetrafluoroethylene "basket" perforated with 1/16 inch (1.6 mm.) diameter holes. The graphite had the same mesh distribution as that used in Example 1.

The holder containing the graphite was immersed into an aqueous 70 weight per cent nitric acid electrolyte. A 1/4-inch (6.3 mm.) diameter carbon rod connected to the positive pole of a variable D.C. voltage rectifier was positioned in contact with the graphite flakes. A second 1/4-inch (6.3 mm.) diameter carbon rod served as a cathode completing the cell. The graphite was electrolyzed at cell potentials ranging from 0.9 volt to 4.8 volts at cell currents ranging from 0.5 amperes to 4.0 amperes and electrolysis temperatures of from about 30 to about 80°C.

A sample of electrolyzed graphite flakes was removed from the cell after current passage equivalent to about 30 ampere hours per pound of graphite. This material was placed in a nickel beaker which had been preheated to about 450°C. The graphite flakes expanded to yield a vermicular product having an apparent bulk density of about 0.2 gram/cc. (12.5 pounds per cubic foot).

The electrolytic action was continued on the remainder of the charge until a total current throughput equivalent to about 60 ampere-hours per pound of graphite had been realized. Expansion of a sample of this material resulted by placing it in a preheated crucible at 450°C. The resulting expanded product exhibited an apparent bulk density of about 4.1 pounds per cubic foot.

After the passage of 95 ampere-hours per pound (204.5 amp. hrs./kg.) of graphite, a similarly heated sample gave an expanded product of about 1.25 pounds per cubic foot (0.02 g./cc.) apparent bulk density. Continuing the anodizing treatment until a current passage equivalent to 200 ampere-hours per pound (440 amp. hrs./kg.) of graphite gave a material which upon heating at 450°C. in the preheated nickel crucible formed a vermicular product having an apparent bulk density of about 0.62 pound per cubic foot (0.01 g./cc.).

A sample of this same unexpanded graphite which had been electrolyzed to the 200 ampere-hours per pound (440 amp. hrs./kg.) of graphite was subjected to direct contact with the flame from a propane torch. The graphite was heated to a temperature of from about 800 to 900°C. whereupon it almost instantaneously expanded into a worm-like product having an apparent bulk density of about 0.1 pound per cubic foot (0.0016 g./cc.).

In a control test wherein a fresh batch of

the same type of graphite flakes was wetted with 70 weight per cent HNO<sub>3</sub> alone, (i.e. without electrolytic action), separated from the acid treating solution and subsequently heated to 450°C. following the expansion technique described for the anodized material, there was no discernible expansion of the so-treated flakes.

In a separate run, about 15 grams of the No. 1 grade natural flake graphite was anodized at 1 ampere current at a potential of about 4.5 volts direct current for 1 hour at a temperature of about 30°C. in an aqueous electrolyte containing about 5 weight per cent HNO<sub>3</sub>. This provided an equivalent current throughput of about 35 ampere hours per pound (77 amp. hrs./kg.) of graphite. The so-treated flakes were heated to about 550°C. in a nickel beaker whereupon the graphite expanded to yield a vermicular product having an apparent bulk density of about 0.066 gram per cubic centimeter (4.15 pounds per cubic foot).

With the nitric acid electrolyte containing about 1.4 weight per cent HNO<sub>3</sub>, anodizing a fresh batch of this same particular graphite at about 30°C. for about 5 hours to a current-time product equivalent to 105 ampere hours at a current range of from 1.5 to 0.5 amperes with subsequent heating of the so-anodized flakes to 400°C. gave an expanded graphite product having an apparent bulk density of about 4.5 pounds per cubic foot (0.072 g./cc.).

About 30 grams of crushed Ceylon crystalline lump graphite (maximum size 2.0 mm.) was similarly electrolyzed in a 41 weight per cent HNO<sub>3</sub> aqueous electrolyte at 3 amperes current for 3 1/2 hours at a temperature of about 30°C. This was equivalent to about 160 ampere-hours per pound (352 amp. hrs./kg.) of graphite. The anodized particulate graphite product was heated to a temperature of about 400°C. whereupon the particles expanded into the typical worm-like mass. This product exhibited an apparent bulk density of about 2.46 pounds per cubic foot (0.039 g./cc.).

Electrolyzing anodically another batch of about 15 grams of the No. 1 graphite flakes in an aqueous 40 weight per cent HNO<sub>3</sub> electrolyte at a cell potential of about 6 volts over a current range of from about 1 to about 4 amperes for a total current time product of about 500 ampere-hours per pound (1100 amp. hrs./kg.) of graphite at from about 30 to about 50°C. gave a material which vigorously expanded at a temperature of about 400°C. into the typical vermicular product. This expanded material had an apparent bulk density of about 0.12 pound per cubic foot (0.0019 g./cc.).

Another sample of this same acid treated material was heated to about 220°C. whereupon it expanded rapidly into the typical low

bulk density vermicular product.

A number of runs were made utilizing either the "basket" cell assembly described in Example 3 or the "porous alumina thimble" cell assembly reported in Example 1. Various acid electrolytes were employed in these studies using No. 1 flake graphite feed stock of particulation as set forth in Example 1. Data and results of these runs are presented in Examples 4—8 inclusive.

#### EXAMPLE 4

About 50 grams of the flake graphite was anodized using as an electrolyte 80 cubic centimeters of concentrated sulfuric acid (98 weight per cent  $\text{H}_2\text{SO}_4$ ) and 200 cubic centimeters of water, i.e.  $\text{H}_2\text{SO}_4$  concentration in the electrolyte of about 42 weight per cent, at a current of about 1.5 amperes, a cell potential of about 5 volts, and electrolysis temperature of about  $30^\circ\text{C}$ . After about 24 hours of electrolysis (total current-time product of 595 ampere-hours per kg. of graphite) the flakes were heated in a nickel crucible to a temperature of about  $500^\circ\text{C}$ . The flakes expanded to a vermicular product having an apparent bulk density of about 1.42 pounds per cubic foot (0.0226 g./cc.).

In a control study, the same type of flake was wetted, without electrolysis, with the 98 weight per cent  $\text{H}_2\text{SO}_4$  containing sulfuric acid. Even with this more concentrated acid, there was no visible expansion of the acid treated material upon subsequent heating to about  $500^\circ\text{C}$ .

#### EXAMPLE 5

About 15 grams of the No. 1 grade natural flake graphite was compacted in the porous alumina thimble and anodized in an aqueous 50 weight per cent  $\text{H}_3\text{PO}_4$  electrolyte at a temperature of from about 40 to about  $50^\circ\text{C}$ ., a current of about 1.4 amperes and a cell potential of about 7.7 volts for about 8.5 hours. The total current throughput was equivalent to 360 ampere-hours per pound (792 amp. hrs/kg.) of graphite. The anodized graphite flakes were heated in a nickel crucible at a temperature of about  $550^\circ\text{C}$ . wherein they expanded into a product having an apparent bulk density of about 10.5 pounds per cubic foot (0.168 g./cc.).

A second batch of the natural flake graphite which had been treated with concentrated phosphoric acid (85 weight per cent  $\text{H}_3\text{PO}_4$ ) without electrolysis did not give any observed expansion when heated at the same temperature in the same manner.

#### EXAMPLE 6

About 10 grams of the No. 1 flake graphite was anodized in an electrolyte consisting of about 20 grams of  $\text{CrO}_3$  dissolved in about 200 cubic centimeters of water. The cell potential was about 3.2 volts and the current was 2 amperes. The total reaction time

was about 1 hour at a temperature of about  $30^\circ\text{C}$ . This is equivalent to about 85 ampere-hours per pound (187 amp. hrs./kg.) of graphite. The anodized flakes were expanded by heating in a nickel crucible at a temperature of about  $500^\circ\text{C}$ . providing a product having an apparent bulk density of about 13.3 pounds per cubic foot (0.213 g./cc.).

#### EXAMPLE 7

About 15 grams of a similar No. 1 flake graphite was anodized in a 48 weight per cent  $\text{HBr}$  aqueous electrolyte at from about 30 to about  $40^\circ\text{C}$ . at a current range of from about 1 to about 4 amperes at a cell potential of from 2 to 10 volts for a period of 4.75 hours. The total current input equivalent was about 135 ampere hours per pound (298 amp. hrs./kg.) of graphite. The so-electrolyzed flakes were heated in a nickel crucible to about  $400^\circ\text{C}$ . giving an expanded vermicular product having an apparent bulk density of about 4.5 pound per cubic foot (0.072 g./cc.).

#### EXAMPLE 8

In an electrolyte consisting of about 50 volume per cent trifluoroacetic acid and 50 volume per cent water, about 15 grams of the same type of graphite flake material was similarly anodized to a current-time product equivalent to about 60 ampere-hours per pound (132 amp. hrs./kg.) of graphite. The actual current employed ranged from about 0.6 to about 2 amperes current at a cell potential of from 2 to 10 volts. Electrolysis was conducted at from about 30 to about  $40^\circ\text{C}$ . Heating of the electrolyzed flake to about  $400^\circ\text{C}$ . gives an expanded graphite product having an apparent bulk density of about 1 pound per cubic foot (0.016 g./cc.). Heating an acid treated sample that had not been electrolyzed provided no visible expansion.

#### EXAMPLE 9

No. 1 graphite (30 grams) was electrolyzed in a cell operating at a cell potential of from 2 to 10 volts at about  $40^\circ\text{C}$ ., and 1 ampere current for about 6 hours. The electrolyte employed consisted of about equal volumes of a mixture of 34 weight per cent  $\text{HCl}$  and about 57 weight per cent aqueous  $\text{HI}$ . The total current throughout was about 91 ampere-hours per pound (200 amp. hrs./kg.) of graphite. Heating of the anodized product to  $400^\circ\text{C}$ . yielded an expanded vermicular product having an apparent bulk density of about 9 pounds per cubic foot (0.144 g./cc.).

#### EXAMPLE 10

Using an electrolyte consisting of about 49 weight per cent aqueous hydrofluoric acid separate charges of about 15 grams of the No. 1 graphite flake were anodized at from about 30 to about  $40^\circ\text{C}$ . for various current time products at a cell potential of about

3.75 volts and a current of about 2 amperes; the so-treated material then was expanded at 400°C. The results of various total current

inputs upon the density of the final expanded product is presented in Table 3.

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TABLE III

Amp—Hours Input		Apparent Bulk Density of Graphite Expanded at 400° C	
Per Pound	Per kg.	Lb./cu. ft.	g./cc.
15	33	4.7	0.0752
30	66	1.1	0.0176
180	396	0.3	0.0048

## WHAT WE CLAIM IS:—

1. A process for preparing expanded graphite of low bulk density characterized by (a) anodically electrolyzing a natural crystalline flake graphite or natural crystalline lump graphite in an aqueous acid or salt electrolyte solution at an electrolyte temperature of from 0 to 80°C., a cell potential of at least 2 volts and utilizing a quantity of electricity equivalent to form 10 to 500 ampere-hours per pound (22—1100 amp. hrs./kg.) of graphite; (b) separating the electrolytically treated graphite from the electrolyte solution, and (c) heating the electrolytically treated graphite at a temperature of from 150 to 1500°C.
2. Process according to Claim 1 wherein the aqueous electrolyte is maintained at a temperature within the range of from 20 to 50°C.
3. Process according to Claim 1 or 2, wherein the cell potential is from 2 volts to 10 volts.
4. Process according to any of Claims 1 to 3 wherein the electrolyte is an aqueous acid selected from nitric acid, sulfuric acid, hydrobromic acid, phosphoric acid, chromic acid, hydrofluoric acid, perchloric acid, trifluoroacetic acid, and mixtures of hydroiodic acid and hydrochloric acid.

5. Process according to Claim 4 wherein

the acid is present in a concentration of from 1 to 70 weight percent.

6. Process according to any of Claims 1 to 3 wherein the electrolyte is a solution of an ammonium or water-soluble metal salt in which the anion is nitrate, sulfate, acid sulfate, bromate, iodate, chlorate, perchlorate, fluoride, bromide, trifluoroacetate or a mixture of chloride and iodide.

7. Process according to Claim 6 wherein the concentration of the salt solution is from 5 weight percent to saturation at the temperature of operation.

8. Process according to any of Claims 1 to 7, wherein the quantity of electricity employed is from 20 to 200 ampere-hours per pound (44—440 amp. hrs./kg.) of graphite.

9. Process according to any of Claims 1 to 8 wherein the heating of the electrolytically treated graphite is carried out at a temperature within the range of from 200 to 1000°C.

10. Process for preparing expanded graphite of low bulk density according to Claim 1 substantially as described with reference to the Examples.

11. Expanded graphite whenever produced by the process of any of Claims 1 to 10.

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